Anthropogenic Disturbance of Element Cycles at the Earth's Surface

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Abstract

The extent to which humans are modifying Earth's surface chemistry can be quantified by comparing total anthropogenic element fluxes with their natural counterparts (Klee & Graedel, 2004). We quantify anthropogenic mass transfer of 77 elements from mining, fossil fuel burning, biomass burning, construction activities, and human apportionment of terrestrial net primary productivity, and compare it to natural mass transfer from terrestrial and marine net primary productivity, riverine dissolved and suspended matter fluxes to the ocean, soil erosion, eolian dust, sea-salt spray, cosmic dust, volcanic emissions and – for helium – hydrodynamic escape from the Earth's atmosphere. We introduce an approach to correct for losses during industrial processing of elements belonging to geochemically coherent groups, and explicitly incorporate uncertainties of element mass fluxes through Monte Carlo simulations. We find that at the Earth's surface anthropogenic fluxes of iridium, osmium, helium, gold, ruthenium, antimony, platinum, palladium, rhenium, rhodium and chromium currently exceed natural fluxes. For these elements mining is the major factor of anthropogenic influence, whereas petroleum burning strongly influences the surficial cycle of rhenium. Our assessment indicates that if anthropogenic contributions to soil erosion and eolian dust are considered, anthropogenic fluxes of up to 62 elements surpass their corresponding natural fluxes.

[Keywords: Anthropocene, biogeochemical cycles, natural cycling, anthropogenic cycling]

Introduction

Humans are moving large amounts of material that have significantly altered the global cycles of elements in Earth's ecosystems.[1] For example, it is estimated that humans are moving 35 Pg (1 Pg = 10^{15} g) of sediment and rock every year through mining and construction activities.[2] Such large displacement of material can significantly disturb the natural flow of elements between major ecosystem reservoirs. The role of humans in altering the physical and chemical processes at the Earth's surface has gained significant attention over the last few decades. Undoubtedly, the alteration is so substantial[3] that 'Anthropocene' has been suggested as an official term to define a new geological epoch in which mankind is reshaping the planet.[4-8]

In a pioneering study Klee and Graedel[9] quantified the magnitude of element fluxes from anthropogenic and natural flows in order to assess the effect of material displacement on the biogeochemical cycles of elements. Although Klee and Graedel,[9] later revised by Rauch,[10] assessed the role of a number of important natural and anthropogenic processes, their assessment did not include several important natural flows, such as eolian dust, cosmic dust, volcanism, and soil erosion. On the anthropogenic side, fluxes from construction activities and human apportionment of terrestrial net primary productivity (HANPP) were omitted. In addition, no statistical analysis was done to incorporate the range of uncertainties in flux estimates. Since these pioneering studies more detailed and comprehensive assessments have been published for individual elements or groups of elements.[11, 12]

This study quantified previously neglected natural and anthropogenic flows, introduced a new method to correct for losses during industrial processing of elements that do not show up in the traditional accounting of mining fluxes, and updated chemical inventories and flux estimates that have not been updated since the pioneering studies.[9, 10] We also included in our assessment

uncertainties of element fluxes to reevaluate the dominance of anthropogenic vs. natural cycling of 77 (noble gases heavier than He and short-lived radionuclides are excluded) of the 92 naturally occurring elements.

Materials and methods

Our approach follows the framework developed by Klee and Graedel[9] in that it compares natural mobilization from weathering, sea-salt spray and primary productivity with anthropogenic mobilization from mining, biomass burning and fossil fuel burning. Geochemical cycling of an element is controlled by processes that mobilize it from one surface reservoir and move it to another. Klee and Graedel define *mobilization* as "the average rate at which the state of a material is transformed from passive (e.g., in rock or soil) to potentially interactive (e.g., in industrial products or in vegetation), with a focus on the pedosphere (where humans literally and figuratively leave their footprints) and the near-surface ocean". The magnitude of mobilization of elements into and out of the reservoirs are called *fluxes*, whereas *flows* are the processes that mobilize elements and transfer them to other reservoirs. Element mass mobilization at the Earth's surface happens through natural and anthropogenic processes. Natural flows include riverine transport of dissolved and suspended particulate matter to the ocean, soil erosion, eolian dust transport, sea-salt-spray, volcanic emissions, extraterrestial dust deposition, hydrodynamic escape from the atmosphere, and net terrestrial and marine primary productivity (NPP). The emerging field of human impacts on marine NPP, either directly (e.g. overfishing) or indirectly (e.g. climate change), has not been included in this study, but deserves scrutiny in future studies.[13] Human flows encompass mining, fossil fuel (coal and petroleum) burning, biomass burning, terrestrial HANPP, and construction of roads, buildings, tunnels and bridges (Figure 1).

Table S1 (Supporting Information) summarizes our natural mobilization calculations (F_N). We build upon the methodology used by the Klee and Graedel[9] and calculate the contribution of individual flows to the total element fluxes by multiplying element concentration (S3, Supporting Information) with annual flux estimates (S1 and S2, Supporting Information). For example, we calculate that 3.4 Tg (1 Tg = 10^{12} g) of copper is mobilized through soil erosion by multiplying the average copper concentration in soils of 0.45 μg/g[14] with an estimated annual soil erosion flux of 75 Pg.[15] Below, we discuss significant revisions to findings in prior studies.[9,10]

Flux of dissolved and suspended particulate matter in rivers

Milliman and Syvitski[16] have shown that rivers deliver about 20 Pg of sediment to the ocean every year. Although the riverine sediment flux that is reaching the ocean is reasonably well constrained, it is questionable whether this flux captures the entire mobilization in watersheds. Large volumes of sediment are sequestered in natural lakes, man-made reservoirs[17], and floodplains.[17, 18] Goodbred and Kuehl,[19] for instance, argue that about 33% of the sediment load of the Brahmaputra River is deposited along the lower parts of the Bengal Delta floodplain without reaching the ocean. Holeman[20] estimated that only about ~10% of the total eroded matter in the United States reaches the ocean, whereas Wason et al.[21] argue that only 1% of the eroded soil in Australia is discharged into the ocean. Recently, Syvitski et al.[22] estimated that over 10% of the suspended sediment flux in rivers has been retained in man-made reservoirs constructed within the past 50 years. Undoubtedly, there is consensus that sediment discharge to ocean does not adequately represent the entire material mobilization on land. A first order comparison of 20 Pg/yr sediment discharged to ocean with a modern estimate of the global rate of annual soil erosion of 75 Pg[15, 23] clearly points out the disparity. The mismatch between

sediment production and the sediment delivered to the sea may be partly explained by anthropogenic perturbation or coastal progradation with subsequent sediment storage in deltas and estuaries. We therefore argue that previous studies[9, 10] have underestimated the total denudation on land, because only river sediment flux to the ocean has been considered.[16] In order to capture the entire mobilization on land, we include 75 Pg/yr of soil losses by wind and water erosion that may have been deposited immediately downslope from the eroding surface without reaching the ocean.

In addition to soil erosion, we include in our assessment ~4 Pg of dissolved matter delivered annually to the ocean by rivers. This estimate is derived by multiplying an average total dissolved solids (TDS) concentration of ~100 mg/l in river water with an annual water discharge of 37,400 km^3/yr.[24] In contrast to previous studies that estimated the entire mobilization on land at 20 Pg,[16] we use an annual flux estimate of ~99 Pg. This includes 20 Pg of riverine suspended sediment load and 4 Pg of dissolved load delivered to the ocean, as well as 75 Pg of soil removal. Total mobilization on land was calculated for each element by multiplying element concentration in upper continental crust[25] with this annual flux estimate.

Eolian dust flux

Asian dust in snow in the French Alps,[26] or a billion tons of African dust annually deposited on the Americas and the Caribbean region[27, 28] are prime examples of physical and chemical fluxes from eolian dust. This natural flow was not included in previous studies.[9, 10] A primary global dust source between 15 $^{\circ}$N to 45 $^{\circ}$N is well-known, with South Africa, Australia, North and South America contributing as dust emitting regions of secondary importance.[29] Estimates of the annual eolian dust emission vary by 2 orders of magnitude from 0.05 to 5.0 Pg/yr.[30] Recently, in an effort to minimize differences between model dust distributions and observations,

Cakmur et al.[31] have narrowed this range to 1.5 - 2.6 Pg/yr. It is generally assumed that 75% of the emitted atmospheric dust is deposited on land, with the remainder deposited on the ocean.[32] However, we consider the entire dust flux as naturally mobilized material without partitioning the mobilized material into different recipient reservoirs. We calculate the contribution of the global dust cycle to the biogeochemical cycles of elements by multiplying element concentration in dust with 2.0 Pg/yr of dust deposition.[31] Unfortunately, the average chemical composition of eolian dust is not well constrained for all of the 77 elements of interest. As dust particles are derived from the deflation of soil, soil composition should serve as a useful proxy for dust chemistry. However, soil composition is spatially heterogeneous, and estimates of globally averaged soil compositions are not available for all the elements of interest. Schutz and Rahn[33] measured the concentration of 40 elements in different types of soil and found that soil composition is within a factor of 2-3 of the average continental crust composition. A more recent study by Lawrence and Neff[14] showed that the major element concentrations (Si, Al, Fe, Mg, Ca, K) in eolian dust are similar (± 20%) to the composition of upper continental crust. We use their estimate for the major elements. For elements not included in the Lawrence and Neff study we use the upper continental crust composition[25] as a suitable proxy, keeping in mind that chemical fractionation during soil formation and dust generation may introduce biases in the chemical flux composition. One could argue that using continental crustal composition as a proxy for dust composition underestimates contributions of elements known to be enriched in dust through anthropogenic activities from smelting, fossil fuel burning, and the proliferation of volatile industrial compounds (e.g. leaded gasoline, reactive nitrogen).[34] As we track such contributions as separate flows in this study, the use of continental crustal composition as a proxy seems justified.

142 Eolian dust may also contain biological materials such as pollen, spores and fur fibers. For
143 the year 2000, bioaerosol emission has been estimated at 0.06 Pg in comparison to 2.0 Pg for
144 mineral dust emission.[35] The organic fraction of the dust may be an important source of
145 biologically cycled nutrients such as N and P,[14] but for most elements it constitutes an
146 insignificant contribution when compared to the total natural mobilization. We therefore do not
147 consider bioaerosols in this study.

148 *Volcanic emissions, accrection of extraterrestrial matter and hydrodynamic escape*

149 Volcanic emissions account for significant chemical fluxes of metals to the atmosphere
150 through passive degassing and intermittent eruptions.[36-38] Here, we only consider emission of
151 aerosols and fine ash into the atmosphere, but not lava flows which mostly remain in the passive
152 realm for centuries or millennia before its components are slowly transferred to the active realm
153 by weathering and erosion. In order to estimate natural mobilization from volcanic sources we
154 use worldwide assessments of annual volcanic element fluxes[36, 37] that are available for 24 of the
155 77 elements of interest. Fluxes for the remaining 53 elements are not considered in this
156 assessment. Our assessment indicates that the chemical fluxes of the highly volatile elements
157 tellurium and mercury account for ~10% of the total natural mobilization, suggesting that
158 contributions of less volatile elements are much smaller.

159 We quantify global fluxes from the accretion of extraterrestial matter on Earth to constrain
160 the role of extraterrestial matter in the biogeochemical cycles of elements. Assuming chondritic
161 composition[39] for the ~0.3 Tg of extraterrestial matter accumulating on Earth annually, we find
162 that contributions from this flow are insignificant when compared to other natural mobilization
163 fluxes, with the exception of osmium and iridium for which accretion of extraterrestrial matter
164 accounts for ~5% of the total natural flux. Our reassessment of natural fluxes also takes into

account the loss of ^{4}He from the atmosphere to outer space,[40] a previously neglected flow that accounts for 65% of the total natural mobilization.

Mining

We summarize our calculations of anthropogenic mobilizations (F_A) in Table S2 (Supporting Information) that include updated annual mine production statistics using the 2011 mineral commodity summaries published by the United States Geological Survey.[41] This update is necessary because of substantial changes in the annual mine production statistics over the last decade. For example, about 2.24 Pg of iron ore were mined worlwide in 2009 compared to 0.7 Pg in 2002.[9]

Correction for Virtual Industrial Production

Mine production statistics tend to underestimate the flux of an element transferred from the geosphere to the anthroposphere because production statistic used in our, and previous, calculations generally reflect the mass of the total purified element brought to market. Losses during industrial extraction, isolation and purification are not considered, but can be substantial. For instance, it has been estimated that only ~5% of indium extracted by mining reaches the market as purified indium metal,[42] leading to an underestimation of the real anthropogenic flux by as much as a factor of 20.[43] Fluxes can be corrected for such losses with a detailed understanding of the industrial processes involved. Alternatively, the geochemical similarities between elements of certain geochemically coherent groups of elements can be used to adjust production statistics to those members of these groups that are most efficiently brought to market. We demonstrate this approach for the rare earth element (REE) and platinum group element (PGE: Os, Ir, Ru, Rh, Pd and Pt) concentrations in their respective ore deposits.

Rare Earth Elements

188 Bastnaesite, monazite and xenotime are the most productive ore minerals for REE.[44]
189 Bastnaesite and monazite are enriched in the light REE (LREE, lanthanum through europium)
190 and exhibit smoothly sloped chondrite-normalized abundance pattern.[44, 45] Xenotime, in
191 contrast, is enriched in heavy REE (HREE, gadolinium through lutetium) and typically shows a
192 chondrite-nomalized pattern that is characterized by a flat HREE segment and a sloped LREE
193 segment.[44] For simplicity, and to demonstrate our correction approach, we assume that
194 bastnaesite and monazite dominate LREE production, whereas xenotime is the main source of
195 HREE. This simplification neglects, among others, the role iron ore mining plays in the
196 production of REE, especially in China.[46, 47] Using this approach, the resulting chondrite-
197 normalized REE production pattern is expected to be relatively smoothly sloped for LREE, and
198 flat for HREE. However, chondrite-normalized REE mineral production data shows a zigzag
199 pattern (Figure 2). We interpret the discrepancy between expected and reported production as an
200 indication of significant losses of certain REE during production. Minimum losses can be
201 quantified by assuming quantitative extraction for lanthanum and lutetium, the two end
202 members, and by fitting a smooth curve between these two elements as a reference for correcting
203 mine production data for losses during industrial processing (Figure 2). To give just one
204 example of the magnitude of the corrections called for by this approach, virtual production (i.e.
205 mass lost during industrial processing) exceeds mass brought to market by a factor of 60 for the
206 element Nd. These are minimum loss estimates because La and Lu may not be extracted with
207 100% efficiency.

208 *Platinum group elements*

209 Principal PGE ore deposits provide a second example of our correction approach.
210 Commercial PGE mining is dominated by mantle-derived ores that are generally characterized

211 by relatively flat chondrite-normalized concentration pattern.[48] Assuming 100% extraction
212 efficiency for palladium, an element predominantly mined for use in automotive catalytic
213 converters, production figures for other PGE are adjusted to their chondritic abundance relative
214 to palladium (Figure 2b). The corrected values indicate that of the total mass transferred from
215 the geo- to the anthroposphere during mining and industrial processing, >90% of Os, Ir and Ru,
216 but only about 5% of Rh and Pt do not reach the market. These are minimum loss estimates, as
217 Pd may not be extracted with 100% efficiency. Significant losses of volatile PGE, especially Os,
218 but possibly also Ru, during industrial processing have been invoked as an explanation for the
219 apparently less radiogenic isotope signature of Os in the upper seawater column.[49] Such less
220 radiogenic $^{187}Os/^{188}Os$ values require input from extraterrestrial or mantle-derived osmium. As
221 extraterrestrial sources are insufficient, a mantle-derived source via industrial processing of PGE
222 ores is consistent with our proposed correction approach. We therefore use corrected PGE and
223 REE production estimates.

224 *Fossil fuel burning*

225 We are using updated estimates for PGE and Re concentration in coal and petroleum that
226 reflect recent analytical developments. This update is necessary because anthropogenic flux
227 estimates in the Klee and Graedel[9] study are based on maximum estimates of 100 ng/g of these
228 elements in coal that reflect the detection limits of the older data sources used. Recently
229 published PGE and Re data on coal[50, 51] and oil[52] show that 100 ng/g overestimates actual
230 concentrations by between one (Re) and four (Ir) orders of magnitude. We assume that the new
231 PGE and Re data on coal and oil are representative of concentrations in hydrocarbons in general.
232 Consequently, the new PGE and Re flux estimates for fossil fuel burning are up to several orders
233 of magnitude lower than previously thought.[9, 10]

234 *Construction activities*

235 Spectacular examples of recent material movements include the 2.0 Pg of sand moved in the
236 construction of Palm Island in Dubai, and displacement of over 0.6 Pg of sediment used to
237 construct the 12.5 km^2 Hong Kong Airport.[2] In spite of this importance, the element mass
238 mobilization from construction has thus far been neglected.[9, 10] Hooke[2] estimated that humans
239 move 35 Pg of Earth annually through mining and construction activities. Recently, Price et al.[7]
240 estimated the worldwide intentional annual movement of sediment by humans at 57 Pg. Since
241 road and house construction accounts for 30% of all material transported by humans[2], we
242 calculated element fluxes from construction activities by multiplying 10.5 Pg/yr of rock and
243 sediment displacement, that is, 30% of the more conservative annual flow estimate of 35 Pg,
244 with average upper continental crust composition.[25]

245 *Human apportionment of terrestrial net primary productivity (HANPP)*

246 Human alteration of photosynthetic productivity on land (HANPP) has received considerable
247 attention over the last few decades.[1, 53, 54] It is estimated that 10-55% of total terrestrial NPP can
248 be ascribed to human activities.[1, 54] In spite of this potential impact, the role of terrestrial
249 HANPP in natural versus anthropogenic element cycling has thus far been neglected.[9, 10] In the
250 year 2000, Haberl et al.[53] estimated that humans mobilized 15.6 Pg of biogenic carbon, or 23.8%
251 of terrestrial net primary productivity. We convert this carbon flux into organic matter flux by
252 multiplying carbon flux by 2.2,[55] and use ~34 Pg as the annual apportionment estimate. We
253 estimate the contribution of terrestrial HANPP to the biogeochemical cycles by multiplying
254 element concentration in plants (Table S3, Supporting Information) with our estimate of 34 Pg
255 anthropogenic HANPP per year. Our assessment shows that chemical fluxes of C, N, Mg, P, K,
256 Ca and Co account for more than 50% of the total anthropogenic mobilization. However,

257 whether HANPP in its totality can be considered human-caused, or just a subset of HANPP that
258 is clearly related to agricultural crop planting and production, deserved further scrutiny.

259 *Treatment of Uncertainties*

260 We assess uncertainties of our estimates by means of Monte Carlo simulations. As the
261 annual flux estimates are calculated by multypling element concentrations with annual flux
262 estimates, annual flux estimates and the element concentrations both require consideration of
263 uncertainties. However, sensitivity analysis of both variables shows that the impact of
264 uncertainties of elemental concentrations on the total fluxes is small compared to the
265 uncertainties of annual flux estimates. For example, estimates of zinc concentrations in average
266 upper continental crust range between 52 and 71 μg/g,[56] whereas estimates of the sediment flux
267 delivered to the ocean vary between 20 Pg[16] and 200 Pg, with the later value based on the
268 premise that river sediment fluxes to the ocean account for only ~10% of the total mobilized
269 material within river basins.[17] In order to estimate the uncertainty of flux estimates, we use the
270 upper and lower estimates of individual flows from literature references, or assume 50%
271 uncertainty, uniformly distributed (Table S1 and S2, Supporting Information). Standard
272 deviations are calculated from one million randomly generated and uniformly distributed flux
273 estimates. Uncertainties are propagated to obtain the final uncertainty of our analysis. We report
274 the ratio of anthropogenic and natural mobilization fluxes and their associated absolute errors
275 and show the logarithms of anthropogenic and natural fluxes ratios in Figure 3.

276 **Results:**

277 Our reassessment of natural versus anthropogenic element fluxes indicates that
278 anthropogenic fluxes of iridium, osmium, helium, gold, ruthenium, antimony, platinum,

palladium, rhenium, rhodium and chromium are greater than the respective natural fluxes. For these elements mining is the major factor of human dominance, whereas petroleum burning strongly influence the surficial cycle of rhenium. Apart from these 11 elements, there are 15 additional elements whose anthropogenic fluxes may surpass their corresponding natural fluxes (Figure 3a). However, uncertainties in the flux calculations prevent us from definitively stating that human activities dominate the biogeochemical cycling of these elements. The anthropogenic fluxes of the remaining elements are smaller than their corresponding natural fluxes, although a significant human influence is observed for many of them (Figure 4). For example, ~20% of annual fluxes of C, N, and P can be attributed to human activities. Such disturbances, though small compared with natural fluxes, can significantly alter concentrations in near-surface reservoirs and affect ecosystems if they are sustained over time scales similar to or longer than the residence time of elements in the respective reservoir.[34, 57] Finally, it is noteworthy to mention that when anthropogenic contributions to soil erosion and eolian dust are considered, anthropogenic fluxes of up to 62 elements may surpass their corresponding natural fluxes.

Discussion:

Following the original definition of mobilization[9] we emphasize that the Klee & Graedel study underestimated natural mobilization, because input from eolian dust, volcanic emissions, soil erosion, accretion of extraterrestrial matter, and loss of light gasses to space were not considered. While the pedosphere was mentioned in the original study, soil was treated as a passive reservoir, a notion that is contrary to the concept of a pedosphere. Anthropogenic mobilization was underestimated, because material displacement from construction activities and human apportionment of NPP were neglected. There are, of course, many additional flows, such

as soil formation, sediment deposition and lithification in the oceans, production and subduction of continental and oceanic crusts, as well as inputs from submarine hydrothermal vents that affect element cycling on Earth. This study, however, focuses on the habitable zone of our planet where the imprint of human activities is obvious. Other, non-surficial flows are therefore not considered. Our approach thus differs somewhat from more recent assessments of the cycling of individual elements, or groups of elements, that include such deep-Earth flows.[11, 12]

In order to assess the relationship between global cycling and surficial cycling, we compare our flux estimates with the recently published Earth's global Ag, Al, Cr, Cu, Fe, Ni, Pb and Zn cycles by Rauch[12] that include element cycling across core-mantle-crust-atmosphere and space. The comparison shows that except for aluminum, all our assessments are within the uncertainty range of these elemental fluxes as quantified by Rauch[12] (Figure 3a). The mismatch between our and Rauch's[12] fluxes for aluminum reflects the fact that global cycling of aluminum is strongly dominated by natural fluxes, particularly crustal production and subduction that account for ~40% of the total natural mobilization. Since we restrict anthropogenic flows to the Earth's surface, additional non-surficial flows will only increase the dominance of natural over anthropogenic fluxes. Global cycling is therefore more strongly dominated by natural processes, particularly if flows between sub-reservoirs, such as between the inner and outer core or the lower and upper mantle, are considered.

Apportioning mixed natural and anthropogenic flows

A potential limitation of our model is that natural flows and the element concentrations used in the calculations may contain a substantial anthropogenic component and vice-versa. While certain flows are undoubtedly natural (e.g., volcanic emission, accretion of extraterrestrial matters, hydrodynamic escape of He), others are clearly anthropogenic (e.g., mining practices,

construction activities and fossil fuel burning). Eolian dust and soil erosion fluxes, however, are affected by natural as well as anthropogenic processes. These fluxes will be discussed in greater detail below.

Eolian dust flux and soil erosion

Eolian dust and eroded soil are most commonly derived from wind erosion and are therefore mobilized by natural processes that transform material from the passive to the interactive realm. However, these natural flows and the concentrations used in the flux calculations may contain a substantial anthropogenic component. For example, mixing of windblown soil with industrial emission and burnt biomass increases the trace metal content of eolian dust[58,59], thereby rendering the dust composition used in our calculations not entirely natural. The flux estimates for the flows may also include human contributions, as studies investigating the impact of land use on dust emission indicate. Moulin and Chiapello[60], for instance, have suggested that land use changes in the Sahel region of Africa have resulted in increased dust deposition in the tropical Atlantic ocean. Similarly, both North and South America have experienced increased dust deposition since the onset of land use changes.[61, 62] Recently, Mahowald et al.[63] estimated that humans are significantly (up to 50%) perturbing the eolian dust cycle.

Soil erosion can also, at least in part, be considered an anthropogenic flow. Unsustainable farming practices and large scale deforestation expose Earth's surface and in the process intensify soil losses.[15] However, it has been difficult to quantify the extent of anthropogenic contribution to soil erosion. Extreme estimates posit that human-induced soil erosion exceeds all other natural soil erosion processes by more than an order of magnitude.[2, 64] To reflect the uncertainty of anthropogenic contributions to soil erosion and eolian dust transport, we consider two scenarios: One treats soil erosion and dust transport as entirely natural (Figure 3a), while the

348 other assumes 50% human influence on both of them (Figure 3b). When such significant human
349 impact is considered, anthropogenic fluxes of 26 elements surpass their corresponding natural
350 fluxes. If, in the extreme, soil erosion were considered a purely anthropogenic flow, only the
351 natural fluxes of Mo, Co, Mg, K, P, C, Na, S, Ca, B, Cd, N, Cl and Br exceeded their
352 corresponding anthropogenic fluxes. In this end-member scenario, anthropogenic fluxes of 62
353 elements surpass their corresponding natural fluxes. Figure 4 compares our results with the
354 previous assessments of Klee and Graedel[9] as revised by Rauch[10] to include a more appropriate
355 flux estimate for sediment transport to oceans than that used by Klee and Graedel.[9] The diagram
356 emphasizes that uncertainties in the magnitude of anthropogenic contributions to soil erosion and
357 eolian dust fluxes limit our ability to apportion more accurately anthropogenic vs. natural
358 contributions to element fluxes related to these important flows. Better apportionments of
359 natural versus anthropogenic contributions to soil erosion (and - though not included in this study
360 - production) were helpful to clarify this issue.

361 In the context of the ongoing discussion about declaring the 'Anthropocene' an official epoch
362 in the Geologic Time Scale[4-8] we demonstrate that, at the Earth's surface, human contributions to
363 the total element mass mobization are significant. The environmental, health, and ecological
364 effects of human contributions are element-specific, and greater anthropogenic dominance does
365 not neccesarily mean greater environmental impact. For example, the cycles of the hazardous
366 elements mercury, lead, cadmium, and arsenic are less anthropogencially dominated than the
367 cycling of osmium and iridium (Figure 4). This study does not attempt to measure the
368 environmental impact of individual elements; it solely emphasizes human contributions to the
369 natural cycling of elements. Considering recent trends in coal, petroleum and mineral
370 exploration, construction activities, and farming practices, it is likely that human influence will

371 continue to increase for all element cycles. Periodic updates of this assessment are therefore
372 desirable to track how severely humans influence natural processes in the habitable zone of our
373 planet.

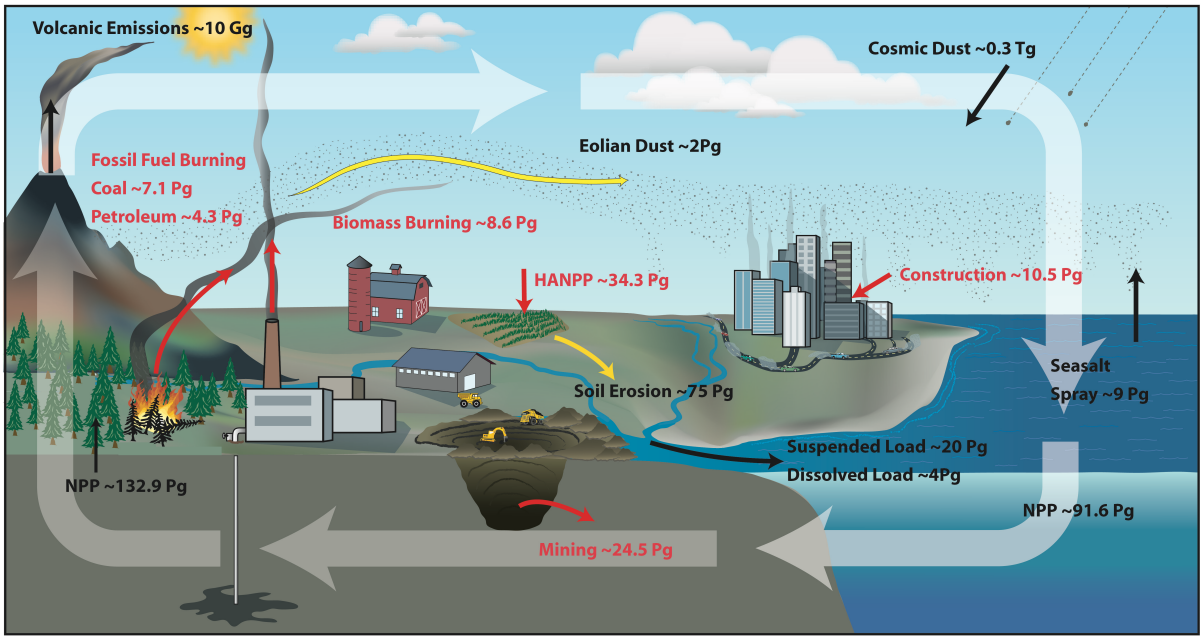
374 **Acknowledgements:**

375 I.S. is thankful for a Woods Hole Oceanographic Institution Postdoctoral Scholarship that
376 supported this work. B.P.-E. acknowledges financial support from a Woods Hole Oceanographic
377 Institution Coastal Ocean Institute Fellowship and also thanks Sarah Jane White (Massachusetts
378 Institute of Technology) for pointing him to her published work on the cycling of indium. We
379 would like to thank the anonymous reviewers for their insightful comments that pushed us to
380 include additional flows and encouraged us to be more quantitative in the consideration of
381 uncertainties. The reviewer's comments significantly improved the manuscript. We thank
382 David A. Dzombak for advice and editorial handling.

383 **Supporting information:**

384 Tables S1 and S2 show natural and anthropogenic element flows, respectively. Table S3
385 summarizes the element concentrations used in natural and human mobilization calculations.
386 The material is available free of charge via the Internet at http://pubs.acs.org.

387



388

389 **Figure 1**: Cartoon depicting natural and anthropogenic flows. Natural flows include terrestrial
390 and marine net primary productivity (NPP), sea-salt spray, riverine dissolved and suspended
391 particulate matter fluxes to the ocean, cosmic dust and volcanic emissions. Anthropogenic flows
392 include mining, biomass burning, fossil fuel (coal and petroleum) combustion, construction
393 activities, and human apportionment of terrestrial net primary productivity (HANPP). Mixed
394 natural/anthropogenic flows include soil erosion and eolian dust. The numbers represent annual
395 flux estimates for the flows. The flux units are Petagram, Pg = 10^{15}g, Teragram, Tg = 10^{12}g, and
396 Gigagram, Gg = 10^{9}g. References for the annual flux estimates are listed in Tables S1 and S2.
397 The contribution of each flow to the total element mobilization was calculated by multiplying
398 element concentration (Table S3, Supporting Information) with annual flux estimates (Table S1
399 and S2, Supporting Information), except for mining and volcanic emissions. Global assessments
400 of individual element fluxes are used for mining and volcanic emissions.[9, 36, 37, 41]

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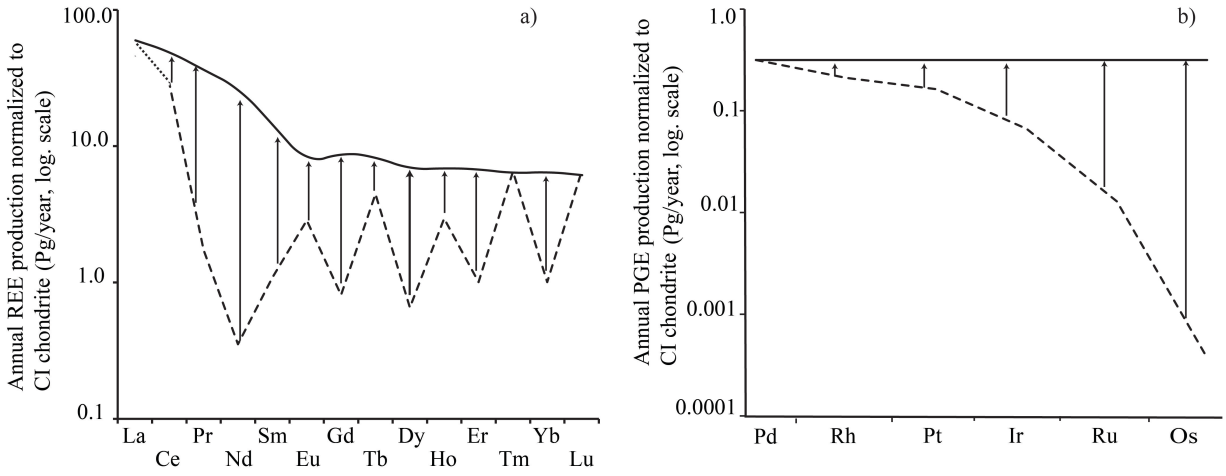

402

403 **Figure 2:** CI chondrite normalized REE (a) and PGE (b) pattern for mine production data
404 (dashed line) compared with expected patterns (solid line) that assume 100% of elements
405 extracted from ore deposits is brought to market. (a) The solid line was constructed with the
406 following assumptions: (i) bastnaesite and monazite are predominantly mined for light REE
407 (lanthanum through europium), while xenotime is mined for the heavy REE (gadolinium through
408 lutetium). (ii) Total removal of bastnaesite, monazite and xenotime ore is assumed to be ~1
409 Tg/yr. Multiplication of the flux estimate with the REE concentrations in ore deposits[44]
410 produces a smooth chondrite-normalized REE pattern. Following that trend, a smooth line was
411 fitted between lanthanum and lutetium. We argue that if the REE production were quantitative,
412 the present mining production data should be corrected upwards. (b) Principal ore deposits of
413 PGE show a flat chondrite-normalized PGE pattern.[48] Assuming 100% production efficiency for
414 Pd, the production values for the remaining PGE need to be corrected upward.

415

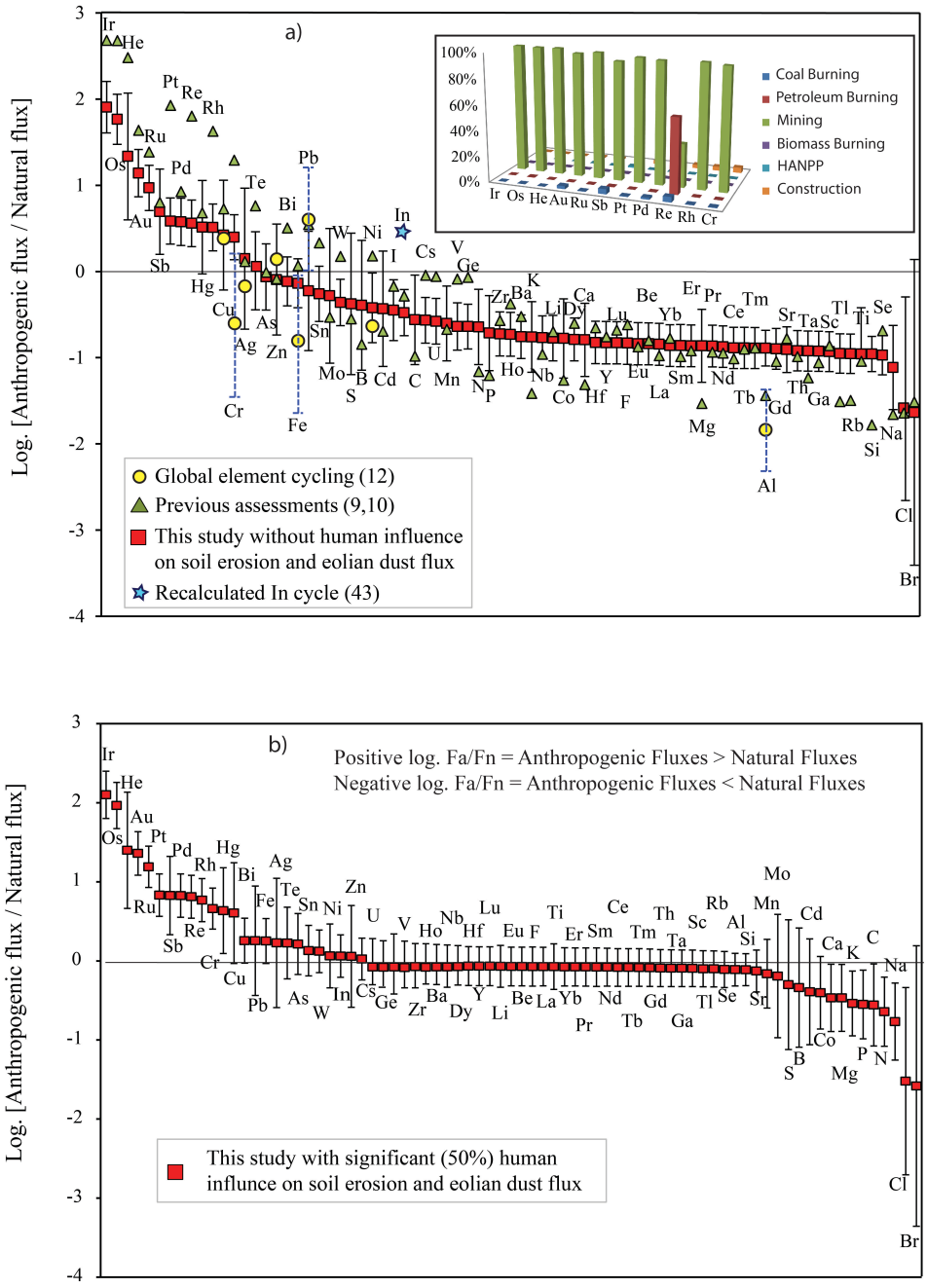

Figure 3A: Comparison of the ratio of anthropogenic and natural mobilization fluxes between Klee and Graedel,[9] as revised by Rauch[10] (green triangles), this study (red squares), and global (including deep earth) element cycling[12] (yellow circles). The blue star shows the recalculated In cycle that takes into account that only 5% of the indium metal extracted from mining is brought to market as indium metal.[43] Positive logarithms indicate human fluxes that are greater than respective natural fluxes. Of the 77 elements considered, anthropogenic fluxes of 11 elements are greater than the corresponding natural fluxes, whereas natural fluxes dominate the cycling of 51 elements. Given the uncertainties in the flux estimates, natural vs. anthropogenic dominance is uncertain for 15 elements. The bar diagram (inset) in the top figure shows the major factors

(in % of total) of human dominance for the eleven human-dominated cycles, generally mining (green bar), and, for Re, petroleum burning (brown bar). **Figure 3B:** Ratios of natural and anthropogenic mobilization fluxes with significant (50%) human influence on soil erosion and eolian dust fluxes. In this scenario anthropogenic fluxes of 26 of the 77 elements considered in this study are greater than the corresponding natural fluxes.

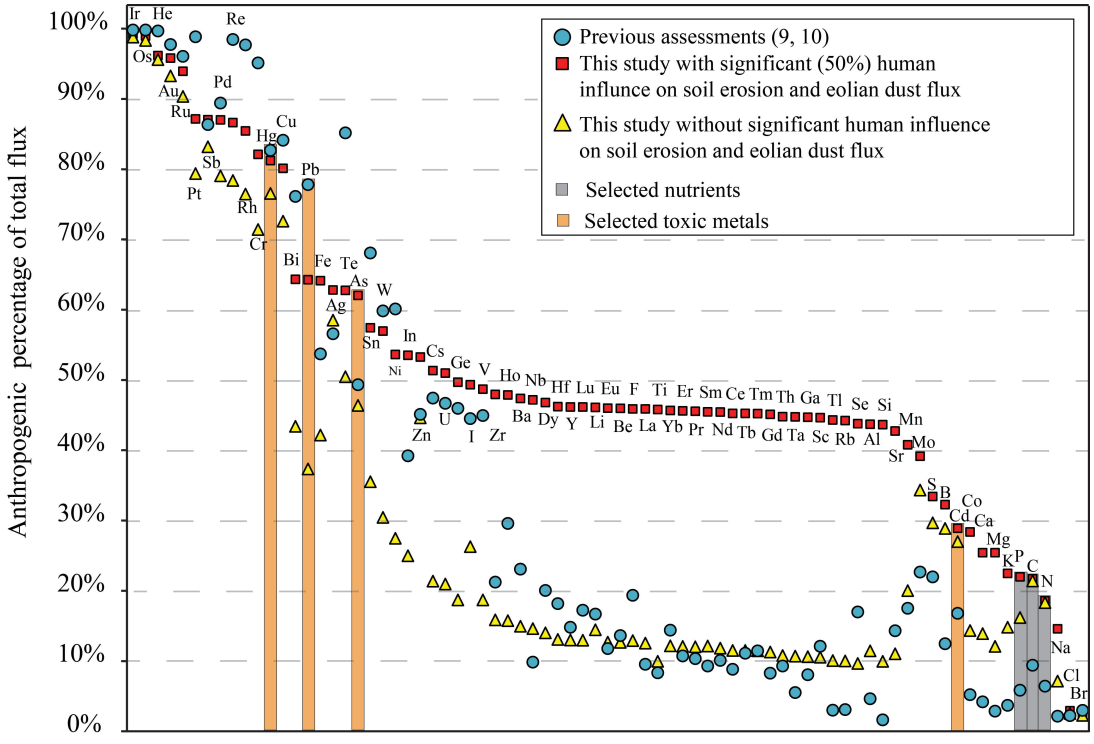

Figure 4: A comparison of relative human contribution (in %) to the total mobilization between this study (red squares: 50% human influence on soil erosion and eolian dust flux; yellow triangles: soil erosion and eolian dust fluxes are considered natural flows) and the revised Klee and Graedel study (blue circles).[9, 10]

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